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Effect of Fe_3O_4 loading on the conductivities of carbon nanotube/chitosan composite films

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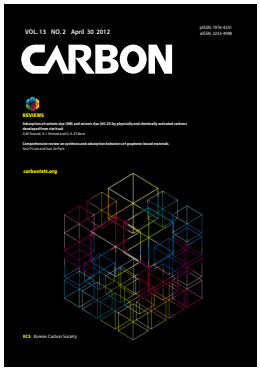

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Abstract

Nanocomposite films were made by a simple solution casting method in which multi-walled carbon nanotubes (MWCNT) and magnetite nanoparticles (Fe_3O_4) were used as dopant materials to enhance the electrical conductivity of chitosan nanocomposite films. The films contained fixed CNT concentrations (5, 8, and 10 wt%) and varying Fe_3O_4 content. It was determined that a 1:1 ratio of CNT to Fe_3O_4 provided optimal conductivity according to dopant material loading. X-ray diffraction patterns for the nanocomposite films, were determined to investigate their chemical and phase composition, revealed that nanoparticle agglomeration occurred at high Fe_3O_4 loadings, which hindered the synergistic effect of the doping materials on the conductivity of the films.

Key words: nanocomposite films, multi-walled carbon nanotubes, magnetite nanoparticles, electrical conductivity

1. Introduction

Carbon nanotubes (CNTs) are one-dimensional nanomaterials that are considered as ideal reinforcing agents for polymer matrices because of their unique structure and properties [1,2]. Electrically conductive composites filled with CNTs have attracted increasing attention for a variety of applications, such as static-charge dissipation [3], electromagnetic interference shielding [4], and actuators [5]. However, CNTs are often in bundles or they are entangled because of very strong intertubular van der Waals attractions, which is the current bottleneck in their application [6].

Chitosan (CS) is a linear polysaccharide synthesized by the deacetylation of chitin, a natural polymer found in the exoskeleton of crustaceans. CS is widely used in biomedical applications, drug delivery, food industry, biotechnology, pharmaceuticals, biomedicine, packaging, wastewater treatment, cosmetics, etc. [7,8]. Another advantage of CS is its solubility in acidic aqueous media. Natural polymers modified with suitable nanofillers have now found potential applications as electrochemical sensors and electrodes [9-13]. CS can be made to possess amphiphilic properties giving it a unique capacity to solubilize hydrophobic CNTs in aqueous solution [14,15]. A key characteristic of the CNT/CS composite is its conductivity, as defined by the charge transfer from one conductive particle to another. Because conduction of electrical charge is established when a network of conductive CNTs reaches a critical percolation threshold density that provides direct electrical contact between particles, the effective conductivity of a CNT/CS composite depends upon many factors, such as size, shape, density, and distribution of CNTs within the CS matrix, as well as chemical interactions between the two materials [16-18].

A Fe_3O_4/CNT/CS composite is expected to have diverse properties because each component contributes different chemical and physical properties to the composite. A Fe_3O_4/CNT/CS composite may find applications in drug delivery, tumor treatment, enzyme en-

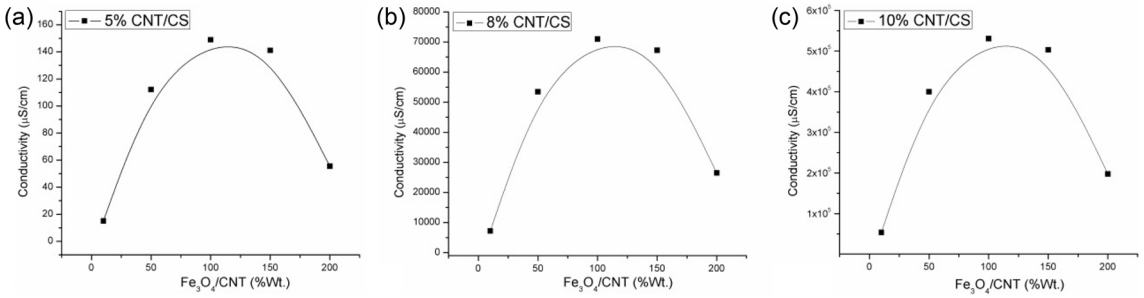

Fig. 1. Effect of Fe_3O_4 loading, expressed as a weight percentage relative to the carbon nanotube (CNT) content, on the conductivity of (a) 5% CNT/chitosan (CS), (b) 8% CNT/CS, and (c) 10% CNT/CS nanocomposite films.

gineering, batteries, electro-magneto rheological fluids, electromagnetic shielding and magnetic recording. In this study, Fe_3O_4/CNT/CS nanocomposite films were prepared by the solution casting method. The main objective was to investigate the synergistic effect of Fe_3O_4 and CNTs on the electrical properties of the nanocomposites. The films were prepared with different concentrations of Fe_3O_4 at fixed quantities of CNTs in order to determine the optimal metal loading for improving conductivity. Subsequently, the electrical conductivity and X-ray diffraction (XRD) patterns were determined for the nanocomposite films.

2. Experimental

CS (average molecular weight = 350 000 $gmol^{-1}$, 90% degree of deacetylation was purchased from Sigma Aldrich. Raw multi-walled CNTs (MWCNTs, CM-95), synthesized using the chemical vapor deposition method, were purchased from Hanhwa Nanotech Co. Ltd., Korea. The MWCNTs had diameters of 10-15 nm, tube length of 10-20 μm and a purity of 95%. Magnetite (Fe_3O_4) nanopowder, (<50 nm particle size [transimission electron microscopy], ≥98% trace metals basis) was purchased from Sigma Aldrich. Acetic acid was used to dissolve CS in distilled water.

CS nanocomposite films containing Fe_3O_4 and CNTs were prepared by the solution casting method [19]. The concentrations of the functional additives (Fe_3O_4 and CNT) were changed in order to evaluate the synergistic effect of Fe_3O_4 and CNTs in the nanocomposite films. Electrical conductivities of the films were measured at room temperature using a ring probe method with a high resistivity meter (MCP-HT 450, Mitsubishi). Wide angle XRD patterns of the Fe_3O_4/CNT/CS nanocomposite films were recorded with a Rigaku Rotaflex (RU-200B) X-ray diffractometer using Cu Kα radiation with a Ni filter. The tube current and voltage were 300 mA and 40 kV, respectively, and 2θ angular regions between 0 and 40° were explored.

3. Results and Discussion

The CS composites were characterized in relation to their conductivity as a function of the CNT to Fe_3O_4 ratio. This was important because the establishment of a highly conductive CNT/CS film requires a network of effective tube-tube contacts. The quality of such a network is ultimately defined by the nanotube concentration and the relative extent of homogeneous (i.e., well-distributed within the matrix) to heterogeneous distribution (i.e., formation of aggregates). The nanotube dimensions limit the effectiveness of electron tunneling across tube-tube contacts. It was also expected that Fe_3O_4 addition would be beneficial to the electrical conductivity of the CNT and the subsequent composite because of the inherent electrical conductivity of Fe_3O_4. Furthermore, the nanoparticles could facilitate electron transfer between nanotubes while being dispersed in the polymer matrix because the composite would acquire more conductive channels and subsequently, a higher metallic character.

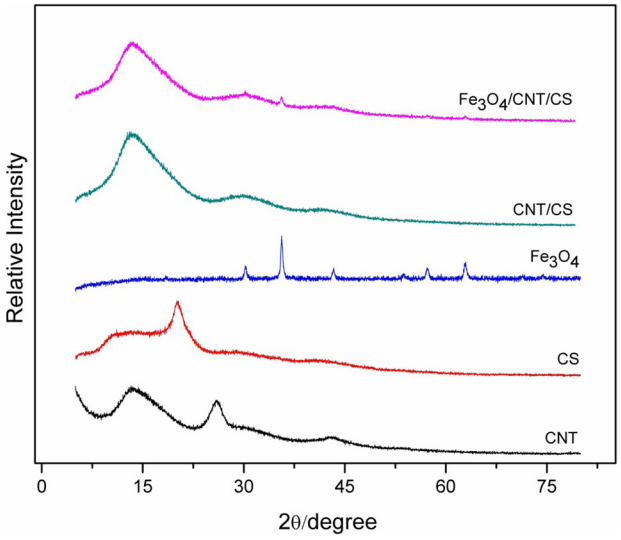

Fig. 2. X-ray diffraction patterns of chitosan (CS), carbon nanotubes (CNTs), Fe_3O_4, and the nanocomposite films.

Fig. 1a shows how the effect of Fe_3O_4 loading, expressed as a weight percentage relative to the CNT content, affects the conductivity of the nanocomposite film. The results clearly indicate the dependence of conductivity on the Fe_3O_4 to CNT ratio. The conductivity improved with increasing Fe_3O_4 content, reaching a maximum at 100% loading, with a subsequent decrease with higher Fe_3O_4 content. It is clearly established that a 1:1 ratio of Fe_3O_4 to CNT in the CS nanocomposite film is the optimal loading for conductivity enhancement. This behavior in conductivity was observed at CNT concentrations of 5, 8, and 10%, as shown in Figs. 1a-c, respectively.

The diffraction patterns of CTS, CNTs, Fe_3O_4 and the nanocomposite films are shown in Fig. 2. In the diffraction pattern

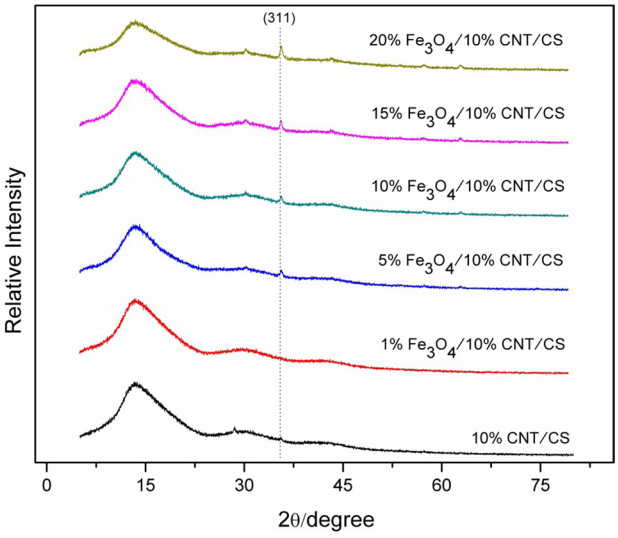

Fig. 3. X-ray diffraction patterns of the nanocomposite films with increasing Fe_3O_4 loading. CNT: carbon nanotube, CS: chitosan.

of CS, one main peak was observed at 2θ = 20° (maximum intensity) corresponding to a characteristic peak of CS chains aligned through intermolecular interactions [19]. The characteristic sharp peak of CNTs at 2θ = 26° represents C (002), which is attributed to the ordered arrangement of concentric cylinders of graphitic carbon in the nanotube [16]. This crystalline peak is not present in the nanocomposite samples, suggesting the dispersion of CNTs into the CS matrix (17). XRD patterns for the Fe_3O_4 nanoparticles displayed characteristic peaks (2θ = 30.1°, 35.5°, 43.1°, 53.4°, 57.0°, and 62.6°). These peaks are consistent with those found in the Joint Committee on Powder Diffraction Standards (JCPDS) database (PDF No. 65-3107). Patterns for the Fe_3O_4/CNT/CS composites revealed the presence of such peaks, indicating that the Fe_3O_4 particles in the composites were pure Fe_3O_4 with a spinel structure.

Fig. 3 clearly shows how increasing Fe_3O_4 loading in the composites resulted in increasing corresponding peak intensities. The figure further shows that neither the CNTs nor CS induced a phase change in Fe_3O_4. Furthermore the results show how the increase in Fe_3O_4 concentration broadened the main peaks, specifically the (400) peak above a Fe_3O_4 to CNT ratio of 1:1, which indicates a higher average particle size of Fe_3O_4 due to increased agglomeration of the nanoparticles. The average particle size, calculated using Scherrer's formula, was approximately 30.79 nm and 46.61 nm for the 1:1 and 2:1 ratios of Fe_3O_4 to CNT, respectively. Hence the decrease in conductivity at higher Fe_3O_4 to CNT ratios was attributed to the agglomeration of the nanoparticles, which hindered the effectiveness of the conductive channels between CNTs; this consequently reduced the conductivity percolation threshold of the composites.

4. Conclusions

Fe_3O_4/CNT/CS nanocomposite films were successfully prepared using a simple solution casting method. A synergistic effect of Fe_3O_4 and CNTs on the electrical conductivity of the nanocomposite films was observed, where by an optimal loading of Fe_3O_4 resulted in a ratio of 1:1 relative to the CNT content of the nanocomposite film. XRD patterns revealed that higher Fe_3O_4 to CNT ratios increased the agglomeration of the Fe_3O_4 nanoparticles, which hindered the synergistic effect on the conductivity.

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